

Control of energy storage of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ nanocrystals by co-activation

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LSO:Ce, LSO:Ce,Dy and LSO:Ce,Yb nanocrystals were synthesized by the sol-gel method. It has been found that the co-activation with Yb^{3+} and Dy^{3+} ions allows the energy storage in a LSO:Ce crystal to be modified and the thermoluminescence and afterglow effects to be controlled. The effect observed is due to electron properties of the co-dopant ion (donor or acceptor) causing the trap charge exchange in a LSO crystal.

Золь-гель методом синтезированы активированные Ce и соактивированные нанокристаллы LSO:Ce,Dy и LSO:Ce,Yb. Установлено, что введение дополнительного иона содопанта (Yb или Dy) позволяет изменять уровень запасаения энергии в кристалле LSO:Ce и тем самым управлять его послесвечением и термолюминесценцией. Наблюдаемый эффект связан с электронными свойствами иона содопанта (донор или акцептор), которые обуславливают перезарядку электронных ловушек кристалла LSO.

Due to a fast $f-d$ luminescence of cerium ions in the visible spectral range, numerous Ce^{3+} -activated crystals are used successfully as scintillators [1]. $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ (LSO:Ce) crystals that possess good scintillation parameters stand out against such scintillators [2]. The LSO:Ce application in modern positron-emission tomographs requires a combination of efficient high energy registration (511 keV) with high time resolution of the scanning system [3]. However, it has been revealed that irradiation of LSO:Ce by photons in the UV spectral range or ionizing radiation causes an effective energy storage that is manifested in the crystal as afterglow and thermoluminescence [4, 5]. This feature restricts significantly the LSO:Ce application.

In [5–7], the nature of electron traps in LSO:Ce crystals was studied in detail. It was revealed that Ce^{3+} ions can be photoionized under some conditions through the excited 5d level. Since the Ce^{3+} excited level is located close to the bottom of the

LSO conduction band, the photoionization can be thermally induced [6]. It was found that the electron traps are formed in the oxyorthosilicate matrix and Ce^{3+} ions are not the centers of electron trap formation [6]. Under optical excitation of Ce^{3+} ions, the activator ions act as electron donors and recombination centers, but not as centers of electron trap generation as it was supposed in [4]. The structure of oxyorthosilicate crystal lattice defects responsible for the electron trap formation and thermoluminescence feature were discussed in [8].

As doped rare-earth ions and electron traps in a LSO:Ce crystal are independent subsystems [6], the trap subsystem can be influenced by the crystal co-activation with other rare-earth elements. The co-dopant selection is defined by its ability to affect the trap subsystem in the crystal, i.e. a co-dopant should possess pronounced electron donor or acceptor properties. In our experiments, Dy and Yb ions were chosen as co-dopants. The $\text{Lu}_{2-x-y}\text{Ce}_x\text{Dy}_y\text{SiO}_5$ (LSO:Ce,Dy) and $\text{Lu}_{2-x-y}\text{Ce}_x\text{Yb}_y\text{SiO}_5$

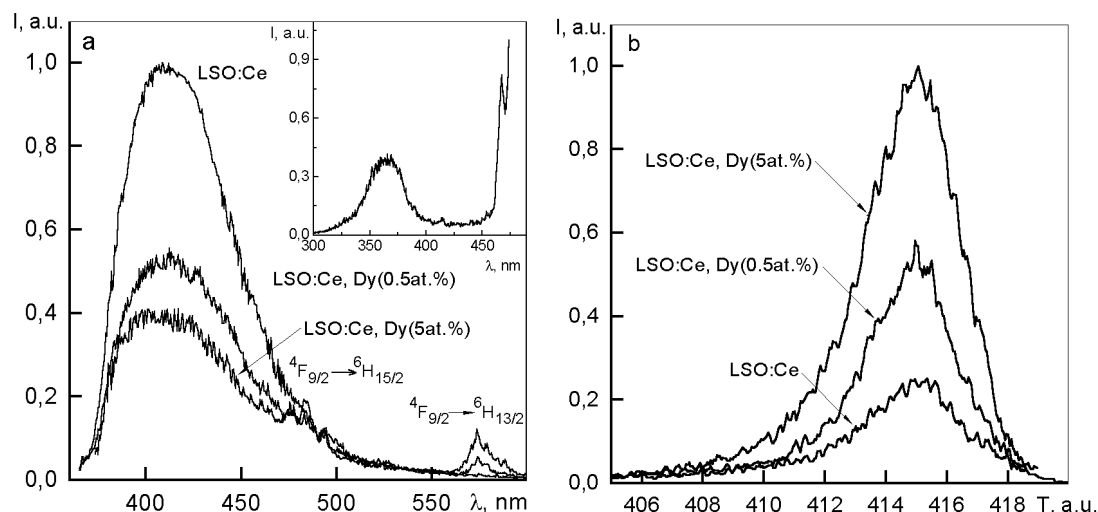


Fig. 1. (a) Luminescence spectrum of $\text{Lu}_2\text{SiO}_5:\text{Ce}$ (1 at.%), Dy at various Dy^{3+} concentrations (0, 0.5, 5 at.%), $\lambda_{exc} = 325$ nm, $T = 300$ K. The inset represents luminescence excitation spectrum of $\text{Lu}_2\text{SiO}_5:\text{Ce}$ (1 at.%), Dy (5 at.%) $\lambda_{reg} = 490$ nm, $T = 300$ K; (b) $\text{Lu}_2\text{SiO}_5:\text{Ce}$ (1 at.%), Dy thermoluminescence spectrum at various Dy^{3+} concentrations (0.5, 5 at.%).

(LSO:Ce,Yb) nano-scale samples were synthesized by the sol-gel method [9] from corresponding Ln_2O_3 ($\text{Ln}=\text{Lu}$, Dy or Yb) oxides. Tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$ was used as SiO_2 precursor. Metal oxides were converted into corresponding nitrates by dissolving in nitric acid. Nitrates of the metals, tetraethoxysilane, ethanol, surfactants were taken in a stoichiometric ratio and stirred at $t = 80^\circ\text{C}$ for 4 h. Ammonia solution was used to increase pH value of the solution to 7 and the mixture precipitation. Then the mixture was dried at 80°C under continuous stirring to paste-like state. The sample obtained was annealed stepwise within the 200–1150°C temperature range. The concentration of cerium was the same for all samples (1 at.%), while the concentration of co-dopants varied within 0.1–5 at.%.

The optically excited luminescence spectra were registered using an automatic spectrofluorimeter on the base of a grating monochromator. The luminescence was excited by a He–Cd laser ($\lambda = 325$ nm) or a Hg-lamp ($\lambda = 365$ nm). The luminescence excitation spectrum of Dy^{3+} in LSO:Ce,Dy was obtained using second monochromator and a xenon lamp to select the necessary excitation wavelength.

Fig. 1 shows the optically excited luminescence spectra of LSO:Ce,Dy. The spectra represent the combination of the well-known band of the Ce^{3+} $5d \rightarrow 4f$ interconfigurational transitions with $\lambda_{max} = 410$ nm and Dy^{3+} $4f^5 \rightarrow 4f^5$ intrastate transitions

within the 460–600 nm range. The increase in dysprosium concentration causes a decrease in cerium luminescence intensity and increase in dysprosium $4F_{9/2} \rightarrow 6H_{15/2}$ and $4F_{9/2} \rightarrow 6H_{13/2}$ luminescence intensity. However, along with an energy transfer process, the direct excitation of Dy^{3+} could be supposed resulting from the spectral overlap of its high-energy 4f states and the laser excitation line ($\lambda = 325$ nm). To verify this supposition, the luminescence excitation spectrum of Dy^{3+} in LSO:Ce,Dy was obtained ($\lambda_{reg} = 480$ nm, see the insert in Fig. 1a). The luminescence excitation spectrum consists of a single wide band that coincides with the Ce^{3+} absorption band in LSO:Ce,Dy. The absorption coefficient on dipole-allowed $4f-5d$ transitions of Ce^{3+} is several orders of magnitude higher than that on dipole-forbidden $4f-4f$ transitions of Dy^{3+} . So, in spite the fact that 4f states of Dy^{3+} are located in the 300–450 nm spectral range, the Dy^{3+} luminescence in LSO:Ce,Dy is excited mainly through the Ce^{3+} ion due to energy transfer.

As it was shown in [8, 10], the energy storage effect is a feature of oxyorthosilicates $\text{Ln}_2\text{SiO}_5:\text{Re}^{3+}$ ($\text{Ln} = \text{Lu}$, Y, Yb, Er, Gd). The location of thermoluminescence maximum depends on a regular Re ion only and is independent of the co-dopant [8]. The variation of co-dopants causes changes in thermoluminescence spectral composition only. In LSO:Ce, thermoluminescence maximum is observed at 340 K [11]. Fig. 1b rep-

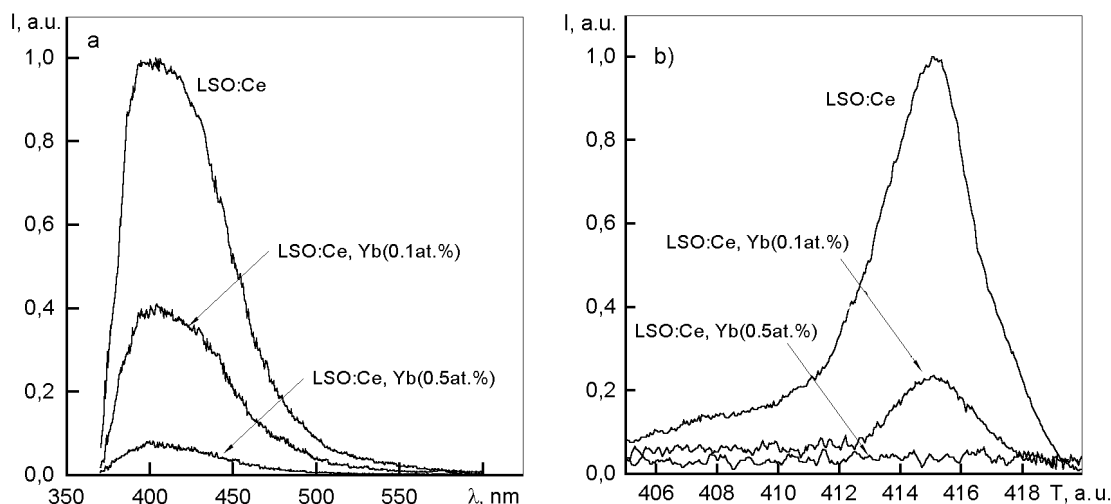


Fig. 2. (a) Luminescence spectrum of $\text{Lu}_2\text{SiO}_5\text{:Ce}(1 \text{ at.}\%),\text{Yb}$ at various Yb^{3+} concentrations (0, 0.1, 0.5 at.%), $\lambda_{exc} = 325 \text{ nm}$, $T = 300 \text{ K}$; (b) $\text{Lu}_2\text{SiO}_5\text{:Ce}(1 \text{ at.}\%),\text{Yb}$ thermoluminescence spectrum at various Yb^{3+} concentrations (0.1, 0.5 at.%).

represents a fragment of the LSO:Ce,Dy thermoluminescence spectrum that corresponds to the specified temperature range. The thermoluminescence was registered in the maximum of cerium luminescence ($\lambda = 410 \text{ nm}$) after irradiation of the LSO:Ce,Dy crystal within cerium absorption band ($\lambda = 325 \text{ nm}$). In the case of the optical excitation in the impurity absorption band, only Ce^{3+} ions act as electron donors charging electron traps that are responsible for thermoluminescence. Figs. 1a and 1b show that increase in Dy^{3+} concentration causes the cerium luminescence decrease and at the same time, increase in thermoluminescence intensity.

The luminescence spectrum of LSO:Ce,Yb consists of the Ce^{3+} luminescence band only (Fig. 2a). Similarly to the LSO:Ce,Dy nanocrystal, increase in Yb^{3+} concentration causes the Ce^{3+} luminescence decrease. However, in contrast to LSO:Ce,Dy, the thermoluminescence intensity decreases and becomes inobservable at Yb^{3+} concentration of 0.5 at.% (Fig. 2b).

Thus, the efficiency of energy storage in the LSO:Ce nanocrystal depends significantly on the co-dopant type (donor or acceptor) and its concentration. As for now, we cannot exactly specify the microscopic mechanisms of the thermoluminescence change in the LSO:Ce crystal depending on

the co-dopant type. We can just note that the effect observed depends on the donor or acceptor properties of the co-dopant and its interaction with electron traps in the crystal involving the conduction band. To develop the adequate physical model, the data concerning the location of impurity and trap energy levels with respect to the crystal band states are necessary.

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Керування запасанням енергії у $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ нанокристалах шляхом співактивування

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Золь-гель методом синтезовано активовані Ce та співактивовані нанокристали $\text{LSO}:\text{Ce},\text{Dy}$ та $\text{LSO}:\text{Ce},\text{Yb}$. Встановлено, що введення додаткового іона співдопанту (Yb або Dy) дозволяє змінити рівень запасання енергії у кристалі $\text{LSO}:\text{Ce}$ і таким чином керувати його післясвітінням та термолюмінесценцією. Ефект, що спостерігається, пов'язаний з електронними властивостями іона співдопанту (донор або акцептор), що обумовлюють перезарядження електронних пасток кристала LSO .